

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

**(19) World Intellectual Property Organization
International Bureau**



(43) International Publication Date
11 July 2002 (11.07.2002)

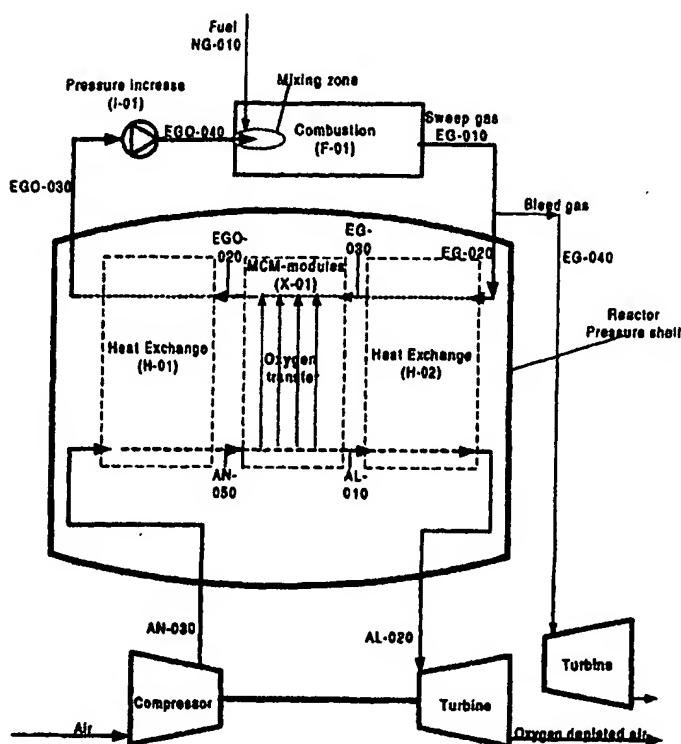
(10) International Publication Number
WO 02/053969 A1

PCT

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|---|------------|--|
| (51) International Patent Classification ⁷ :
F23L 7/00, B01D 53/22, F02C 3/34 | F23C 9/00, | (72) Inventors; and
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| (21) International Application Number: PCT/NO01/00499 | | |
| (22) International Filing Date:
19 December 2001 (19.12.2001) | | |
| (25) Filing Language: | English | |
| (26) Publication Language: | English | (74) Agent: JOHNSEN, Venche, Høines; Norsk Hydro ASA, N-0240 Oslo (NO). |
| (30) Priority Data:
200006690 29 December 2000 (29.12.2000) | NO | |
| (71) Applicants (for all designated States except US): NORSK HYDRO ASA [NO/NO]; N-0240 Oslo (NO). ALSTOM POWER SWEDEN AB [SE/SE]; S-612 82 Finspång (SE). | | (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, |

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- (54) Title: A DEVICE FOR COMBUSTION OF A CARBON CONTAINING FUEL IN A NITROGEN FREE ATMOSPHERE AND A METHOD FOR OPERATING SAID DEVICE**



(57) Abstract: The present invention relates to a device for combustion of a carbon containing fuel in a nitrogen free atmosphere, and a method for operating said device. The device may be integrated with a power generation plant (i.e. gas turbine(s)) to obtain an energy efficient process for generation of power with reduced emission of carbon dioxide and NOx to the atmosphere. Furthermore, the device may be integrated with a chemical plant performing endothermic reactions.

WO 02/053969 A1



SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

Published:

— with international search report

- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

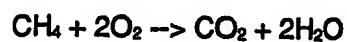
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A device for combustion of a carbon containing fuel in a nitrogen free atmosphere and a method for operating said device.

The present invention relates to a device for combustion of a carbon containing fuel in a nitrogen free atmosphere and a method for operating said device.

The device may be integrated with a power generation plant (i.e. gas turbine(s)) to obtain an energy efficient process for generation of power with reduced emission of carbon dioxide and NO_x to the atmosphere. Furthermore, the device may be integrated with a chemical plant performing endothermic reactions.

Conventional combustion processes, used for carbon containing fuels, will in addition to producing the main end products carbon dioxide and water (steam), generate a considerable amount of heat (heat of combustion). A conventional combustion reaction between e.g. methane and oxygen will generate approximately 804 KJ per mol methane:



When this combustion process is integrated with e.g. a power generation plant (i.e. gas turbines) or a chemical plant performing endothermic reactions, it is crucial that the total energy loss from the combustion process is as low as possible.

Furthermore, due to the environmental aspects of CO₂ and NO_x it is crucial that the emission of these components to the atmosphere is considerably reduced compared to conventional processes. Conventional combustion processes produce an exhaust gas with a CO₂-concentration between 3 and 15% dependent on the fuel and the combustion- and heat recovery process applied. The reason the concentration is this low is because air comprises about 78% by volume of nitrogen. In high-temperature combustion processes in air, nitrogen will react with oxygen and produce the environmental hazardous gas pollutant NO_x.

A reduction in the emission of carbon dioxide to the atmosphere makes it necessary to either separate the carbon dioxide from the exhaust gas, or raise the concentration in the exhaust gas to levels suitable for use in different chemical processes or for injection in e.g. a geological formation for long term deposition or for enhanced recovery of oil from an oil reservoir.

CO₂ can be removed from cooled exhaust gas, normally discharged at near atmospheric pressure, by means of several separation processes, e.g. chemical active separation processes, physical absorption processes, adsorption by molecular sieves, membrane separation and cryogenic techniques. Chemical absorption, for instance by means of alkanole amines, is considered as the most practical and economical method to separate CO₂ from exhaust gas. These separation processes consume energy and require heavy and voluminous equipment. Applied in connection with a power generation process, these separation processes will reduce the power output with 10% or more.

An increase of the concentration of CO₂ in exhaust gas from a combustion reaction to levels suitable for use in different chemical processes or for injection in e.g. a geological formation for long term deposition or for enhanced recovery of oil from an oil reservoir is possible by burning the carbon containing fuel with pure oxygen instead of air.

Commercial air separation methods (e.g. cryogenic separation or pressure swing absorption (PSA)) applied for producing pure oxygen require 250 to 300 KWh/ton oxygen produced. If these methods are used for supplying oxygen to a combustion process in a gas turbine cycle these methods will reduce the net power output from the gas turbine cycle by at least 20%. The expenses of producing oxygen in a cryogenic unit will increase the price of produced electric power substantially and may amount to as much as 50% of the cost of the electric power.

However, a less energy demanding method than these separation methods is known from the European Patent Application 658 367- A2. The patent application describes an application of a mixed conducting membrane (MCM) integrated with a gas turbine system and where the membrane separates oxygen from a heated air stream.

The mixed conducting membrane (MCM) is defined as a membrane made of materials with both ionic and electronic conductivity. The membrane selectively transports oxygen. The driving force through the membrane is proportional to the logarithmic relation between oxygen partial pressures; $\log (pO_2(I)/pO_2(II))$, where (I) represents the oxygen delivering side (air) of the membrane and (II) represents the oxygen receiving side of the membrane. To keep a high transport rate (flux) of oxygen it is important to keep a low partial pressure on the oxygen receiving side.

Thus, to further improve the efficiency of this membrane process, a sweep gas is applied to reduce the partial pressure of oxygen on the oxygen receiving side of the membrane and thereby increase the flux of oxygen through the membrane; as e.g. described in US 5562754 and NO-A-972632.

To obtain practical applications of mixed conducting membranes (MCM) when applied as an oxygen supplier in a combustion process the following criteria are essential:

- a) The driving force of the oxygen transport through the membrane expressed as the logarithmic relation between oxygen partial pressures; $\log (pO_2 (I)/pO_2 (II))$, has to be kept at a high level.
- b) The membrane has to operate at high temperature levels ($>600^\circ\text{C}$) to achieve a sufficient oxygen flux through the membrane. Thus air or any other gases in contact with the membrane must have a high temperature.

To ensure that the driving force through the membrane is kept at a high level oxygen on the oxygen receiving side of the membrane has to be:

- i) transported away from the membrane surface, by applying a sweep gas, or
- ii) consumed by a chemical reaction (e.g. a combustion process) directly on the oxygen receiving side.

This implies that the device which shall perform an energy efficient combustion in a nitrogen free atmosphere must be designed to operate under process conditions as mentioned above. There remains therefore a need for such a device and a method for operating said device that is not described in the prior art.

The main object of the present invention was to provide a device effective to achieve combustion of a carbon containing fuel in a nitrogen free atmosphere.

Another object of the present invention was to provide a device effective to achieve a combustion process resulting in an exhaust gas with a high concentration of CO_2 and a low concentration of NO_x .

Furthermore, another object of the invention was to provide a method for operating said device.

Yet another object of the invention was to provide a plant and a method for an energy efficient generation of power.

Still yet another object of the invention was to provide a plant and a method for generation of power with reduced emission of carbon dioxide and NO_x to the atmosphere.

The inventors found that the described objects were fulfilled by utilizing a device where one or more mixed conducting membrane module(s), one or more heat exchange module(s) and one or more combustion chamber(s) were enclosed within a hollow shell (a pressure vessel) defining an enclosure. The device may further be integrated with gas turbine(s) in a plant for generation of power. The device may also be integrated with a chemical plant performing an endothermic reaction to supply necessary heat to the reaction.

The mixed conducting membrane(s) (MCM) which is utilized in the device according to the present invention will at conditions described above (a) and b)) transport oxygen from an oxygen delivering gas (e.g. air) to an oxygen receiving gas. The oxygen receiving gas has a lower partial pressure of oxygen than the oxygen delivering gas. To the oxygen receiving gas a carbon rich fuel (e.g. natural gas) is added and a heat generating combustion reaction between oxygen and added fuel takes place.

Combustion of natural gas with pure oxygen will produce an exhaust gas containing the two main products carbon dioxide and water (steam). According to the present invention the exhaust gas is utilized as the oxygen receiving gas. The oxygen rich gas stream (i.e. the oxygen enriched exhaust gas) is fed to the combustion chamber and applied as oxidant in the combustion reaction. Thus, a production of the environmental harmful NO_x gas is avoided.

The thermal energy produced by the combustion reaction is by means of heat exchanger(s) utilized to heat air fed to the MCM-module(s) as well as to heat oxygen depleted air leaving the MCM-module(s) before it may enter a power generation turbine or a chemical plant performing an endothermic reaction.

Thus the air stream fed to the membrane is heated without producing CO₂ or NO_x in the stream. In the combustion reaction almost all oxygen is consumed and thus the exhaust gas, now having a very low partial pressure of oxygen, can be re-circulated to the MCM as a sweep gas picking up oxygen before entering the combustion chamber again. Thus we have a continuous combustion. From the exhaust gas a bleed stream has to be taken out to balance the added fuel and oxygen received to prevent accumulation of mass. This bleed gas leaving the device at elevated pressure and temperature could also be fed to a power generation system (turbine). In the turbine the pressure of the bleed gas is decreased and further cooled to condense almost all steam to water. Thus the gas flow will consist mainly of carbon dioxide. This carbon dioxide gas flow has to be compressed to a pressure that allows injecting in an underground reservoir, a reservoir that could be an aquifer layer or a gas or oil reservoir. These reservoirs should be qualified for ensuring long term deposition.

As mentioned above the exhaust gas is utilized as a sweep gas to pick up oxygen in the membrane module(s) and transport oxygen to one or more combustion chambers where fuel is added. The heat generated in the exhaust gas should in an efficient way be transported to the air stream, and in such a way, that leakage between sweep gas and air is prevented or minimised to an acceptable level.

Furthermore, the inventors found that by utilizing a multiplate or a multichannel structure as a MCM-module and/or as a heat exchange module a very efficient device was achieved. Multichannel structures are found to be the most advantageous due to the fact that they can be extruded in one piece (i.e. a

monolith) and thus a large surface area in one piece is obtained. Most preferably both the heat exchange module(s) and the MCM-modules are made of a ceramic material that is able to withstand the present process conditions (atmosphere, temperature and pressure).

Such structures, especially with channel diameter below 10 mm, give a very high surface area/unit volume. By preparing every second row of channels by inlet slots as described in US Patent 4271110 a simplified manifold system to every second row of channels could be achieved and thus give a low leakage rate probability between the air side and the oxygen receiving side.

To obtain a largest possible surface area for heat exchange and/or oxygen transfer (when utilized as a MCM-module), the channels should be very small and every air channel should be surrounded by (i.e. have common walls with) the other gas (i.e. sweep/exhaust gas). Such a configuration needs a very complicated system for leading the two gases (manifolding) to each adjacent channel.

According to the present invention such multichannel monolithic structures are connected or linked together in such a way that the MCM-module is installed between two heat exchange modules. Furthermore, these modules are installed in a pressure vessel hereinafter defined as the reactor. Such a system will ensure that the MCM is able to operate at a defined temperature higher than the temperature in the air stream fed to the system and below the temperature of combustion (i.e. the exhaust gas temperature from the combustion chamber).

Another important feature of the present invention is the flow pattern of the two gas streams. The first gas stream (the air stream) has a flow from inlet to outlet of the reactor that follows longitudinal to the direction of channels in the monolithic structures (i.e. heat exchangers and MCM). This means that the gas enters and leaves the open channels from the short ends and flows through an open room or

closed structure that connects these ends. The second gas stream has a flow direction in and out of the side slots of the monolith, through bypass rooms or connectors to the side slot of the adjacent monolithic structures. These bypass rooms are surrounding the inner open room of the first gas.

Such a flow system of the gases will allow one of the gases, here the second gas, to leak and fill all available space or "empty" room of the reactor. The requirement for a gas tight sealing is then reduced for the first gas only to be a sealing towards the second gas (not to the "empty" space of the reactor) located at the inner coupling connectors between the monolithic structures.

This feature is very important because a controlled leakage of gas is necessary to build up and equalise the pressure inside the reactor house, and only one of the gases is allowed to leak to prevent mixing. This controlled and necessary leakage allows a flexible sealing of defined leakage rate for the bypassing connectors of the second gas. Flexibility to avoid thermal stress in connecting parts/monolithic structures is very important to prevent fatal cracks.

By filling the reactor with gas of almost the same pressure as the gas inside the monolith channels only the outer pressure shell of the reactor has to withstand the absolute or total pressure of the process. The pressure on the monolith walls is then reduced to withstand the differential pressure between the two gases (Gas 1 and Gas 2 in Figure 3).

The scope of the invention and its special features are as defined by the attached claims.

The invention will be further explained and envisaged in the following figures.

- Fig. 1 shows a sketch of one embodiment of the device according to the present invention including its functional parts as heat exchange module, MCM-module and combustion chamber. Also included is a pressure booster, here shown as a jet ejector driven by high pressure (HP) steam. In this embodiment the modules are all installed within the reactor.
- Fig. 2 shows another embodiment of the device according to the present invention including the same functional parts as heat exchange module, MCM-module as well as a combustion chamber and a pressure booster, but in this embodiment the combustion occurs in a separate vessel connected to the reactor. The pressure booster is installed in the connecting pipes, preferably prior to the combustion chamber where the sweep gas has its lowest temperature.
- Fig. 3 shows a sketch of a multichannel monolith structure utilized as a MCM-module and/or as a heat exchange module.
- Fig. 4 shows one embodiment of the reactor with the different modules as well as the other functional components in the reactor.
- Fig. 5 shows different shapes of connectors between the MCM- and the heat exchange modules as well as different methods applied for sealing of the connectors between the modules.
- Fig. 6 shows one embodiment of the device according to the present invention where the combustion chamber is installed outside the reactor as well as some of the internal components taken out of the reactor for the purpose of better illustrating these individual components.

Fig. 7 shows a more detailed illustration of the whole device according to the present invention as well as the individual components of the reactor.

Fig. 8.1 shows one embodiment of a plant for generation of power where the device according to the present invention is integrated with gas turbines.

Fig. 8.2 shows another embodiment of a plant for generation of power where the device according to the present invention is integrated with gas turbines and where more than one reactor have a common combustion chamber.

Fig. 9.1 shows one embodiment of the device according to the present invention where each process stream is given a tag number according to Table 1.

Fig. 9.2 illustrates the internal flow path of the air in the reactor.

Figure 1 shows a principal sketch of the device according to the present invention where the process streams and the important process units (H-01), (X-01), (H-02), (F-01) and (I-01) are shown. The units are all installed inside the reactor pressure shell which is in this example identical to the device shell. The figure shows that an oxygen containing gas stream (here air) is conducted through a compressor. The compressed air stream (AN-030) is further fed to the heat exchange module (H-01) where it is heated (AN-050) before entering the mixed conducting membrane module (X-01) in which oxygen is separated from the air stream resulting in an oxygen depleted air stream (AL-010). The oxygen depleted air stream (AL-010) enters the heat exchanger (H-02) for further heating before leaving the device (AL-020). The depleted air stream (AL-020) may be fed to a power generation turbine or a chemical plant performing endothermic reactions. A

sweep gas (EG-020) is fed to the MCM-module (X-01) and is picking up oxygen at the oxygen receiving side of the membrane and further transported through heat exchange module (H-01). The oxygen enriched gas stream (EGO-030) is then pressurized in a pressure booster (I-01) before entering the combustion chamber (F-01). The combustion chamber (F-01) where fuel (NG-010) is added and burned is in this example installed inside the reactor pressure shell. The combustion gas or exhaust (EG-010) is now almost oxygen free due to combustion in (F-01).

A part of the hot combustion product or exhaust gas (EG-010) is taken out as a bleed stream (EG-040) to prevent accumulation of mass in the reactor while the rest of the product gas is fed to the heat exchange module (H-02) and heated to the operational temperature of the membrane. In the membrane module stream (EG-020) is acting as a sweep gas. The hot and oxygen enriched sweep gas stream (EGO-020) is fed to the heat exchange module (H-01) to heat the incoming gas stream (AN-030). The heated air stream (AN-050) is entering the MCM-module (X-01) at the operational temperature of the MCM-modules (X-01). A pressure booster (I-01) has to be installed to enhance circulation in the sweep gas loop and ensure a continuous combustion. In Figure 1 this is a jet pump driven by injection of high pressure (HP) steam. The jet pump has the advantage of no moving parts and might be built in a material (i.e. ceramic) that can withstand very high temperatures. For power generation the oxygen depleted gas stream (AL-020) and the bleed gas stream (EG-040) may be fed to gas turbines to generate power. The bleed gas (EG-040) containing the main combustion products ($\text{CO}_2 + \text{H}_2\text{O}$) will have a high temperature (combustion gas temperature). To generate power directly from the stream a gas turbine capable of handling the CO_2 and H_2O mixture is needed. Another power generating alternative for this stream is to cool down the gas to a temperature $<550^\circ\text{C}$ where a conventional steam turbine can be used. This can be done by injecting water to stream (EG-040) or heat exchange with the incoming "cold" air stream (AN-030).

Figure 2 shows another embodiment of the device according to the present invention where the pressure booster (I-01) and the combustion chamber (F-01) are installed outside the reactor pressure shell but within the device shell. This feature contributes to simplify the construction of the device. The advantage of installing (I-01) and (F-01) outside the reactor is to facilitate the maintenance work and makes it possible to apply cooling apparatus. Thus a rotary pressure increasing machine can be used as a pressure booster (I-01) as envisaged in this figure. The flow path in this embodiment is the same as in the embodiment shown in Figure 1. The only difference is that no high pressure (HP) steam is injected (because no jet pump is used), but this will not amend the principle flow pattern. Injecting high pressure (HP) steam as shown in Figure 1 will reduce the net power generation efficiency of the process and thus a rotary machine as shown in Figure 2 is with respect to efficiency more advantageous.

An external combustion chamber will also simplify the fuel (NG-010) injection system and makes it easier to upscale the device as will be shown in Figure 8.

Figure 3 shows a multichannel monolith structure which, according to the present invention might preferably be utilized as both a heat exchange module and a membrane module. As mentioned above, such structures are advantageous mainly because of their simple way to be manufactured. However, the present invention is not restricted to application of such structures only and other configurations (e.g. plates) may be an alternative.

According to Figure 3, using stream notation as in Figures 1 and 9, Gas 1 represents gas streams (AN-030) and (AN-050) if the monolith structure is module (H-01), gas streams (AN-050) and (AL-010) if the monolith structure is module (X-01). If the monolith structure is module (H-02), then Gas 1 is gas streams (AL-010) and (AL-020).

Gas 2 represents the gas streams (EGO-020) and (EGO-030) if the module is (H-01), the gas streams (EG-030) and (EGO-010/020) if the module is (X-01) and gas streams (EG-020) and (EG-030) if the module is (H-02).

Gas 1 follows the straight path through the channels and is thus always fed in and let out from the open rows of channels at the monolith ends. Gas 2, normally the sweep gas, is always fed in and taken out from the open slots in the side wall of the monolith structures. Since these monolithic structures preferably will be made by extrusion, all channels will be of the same length. The inlet and the outlet slots of Gas 2 must be made after extrusion by machining every second column of channels as visualised on the figure. After machining down to the preferred depth the open row of channels (made by machining) has to be closed by a sealing in such a way that a sufficient opening area for the side slot is kept (inlet and outlet for Gas 2).

The problem of preventing leakage in the manifold system of two different gases leading in and out of the multichannel monolithic structures is minimised by making these inlet and outlet slots as described and shown in Figure 3.

According to the present invention a channel diameter below 10 mm is used. A diameter between 1 and 8 is preferred.

Figure 4 shows one embodiment of the reactor as described in Figure 2, where the combustion chamber and the pressure booster are mounted outside the reactor shell. In the figure the connecting flanges for the inlet (EG) and the outlet (EGO) of the sweep gas stream as well as the inlet (AN) of the air stream and the outlet (AL) of the oxygen depleted air stream are shown. Inside the reactor the flow path of these streams is visualized by dotted lines. Heat exchanger (H-01), MCM-modules (X-01) and the outlet heat exchanger (H-02) are fixed together by the connectors between (H-019, (X-01) and (H-02). These connectors are prefer-

ably glass sealed, before installed in the reactor, to ensure no leakage and thus will be one whole part (i.e. sealed together). During heating this whole part has to be allowed to expand. This will be further described in Figure 7.

Figure 5 shows alternative shapes for the connectors between the (X-01) and (H-01/H-02). Thus (H-01) and (X-01) as well as (X-01) and (H-02) could be connected and sealed to each other by different components as shown. The most important factor is to have a tight sealing without leakage between the inner gas (i.e. Gas 1 as described in Figure 3, preferably air) and the outer gas (i.e. Gas 2 described in Figure 3, preferably sweep gas).

Figure 6 shows one embodiment of the device according to the illustration in Figure 2, where the combustion chamber (F-01), as well as the pressure booster (I-01) are installed outside the reactor. Fuel (NG) is injected in the low temperature zone prior to (I-01) to ensure a good mixing with the oxygen enriched sweep gas (EGO) before entering the combustion chamber (F-01). Due to a too low temperature the combustion, at least partly, might be enhanced by a catalyst. The sweep gas stream (EGO) leaving (H-01) is cooled down by the air stream (AN) and has its lowest temperature before (I-01). The pressure in the stream (EGO) is increased by means of (I-01) before entering the combustion chamber (F-01) outside the reactor. In (F-01) oxygen in stream (EGO) reacts with added fuel and a combustion is obtained. In the combustion nearly all oxygen is consumed. Thus the exhaust gas (EG), mainly containing the reaction products (CO_2 and H_2O), will have a low content of oxygen. (EG) enters the second heat exchanger (H-02) where it is heating the oxygen depleted air stream (AL) leaving the reactor.

(EG) is thus somewhat cooled down by (AL) in (H-02) before it enters the membrane module(s) (X-01). In (X-01) (EG) acts as a sweep gas picking up oxygen transferred through the membrane wall from the air side. The oxygen enriched sweep gas leaving (X-01), now named (EGO), is then entering the first heat exchanger (H-01) where the air stream (AN) is heated and the stream (EGO)

is cooled. Thus a cooled oxygen containing sweep gas (EGO) is now returning via (I-01) to (F-01) and thus an exhaust/sweep gas loop is obtained enhancing a continuous combustion.

Either from the oxygen enriched sweep gas (EGO) or from the exhaust gas (EG) a bleed gas has to be taken out to prevent accumulation of mass in the sweep gas loop due to the oxygen transfer from the air and the addition of the fuel. Example of bleed gas outlet is shown in Figures 8.1 and 9.1.

Also shown in Figure 6 are some of the individual components of the reactor.

Figure 7 shows a more detailed embodiment of the device according to the present invention.

Reactor pressure vessel 1 contains the low temperature heat exchanger 9, the high temperature heat exchanger 19 and the MCM-modules 15. Thus all other parts are built up around these units 9, 15 and 19 which ensure good heat transfer (from sweep/exhaust gas to air) and oxygen transfer (from air to sweep gas). The parts 8, 14 and 18 are used to make a round shape at the outer wall of the heat exchangers and MCM-modules to ensure less complicated sealing. These parts could also be made with channels in such a way that they can be used as heat exchangers 8 and 18 or as MCM-modules 14. The individual parts 10, 11, 12 and 13 will fit together and make the connection between the low temperature heat exchanger 9 and the MCM-modules 15 as shown in Figure 5.3. In the same way the individual parts 16, 17, 20 and 21 will make the connection between the MCM-modules 15 and the high temperature heat exchanger 19. The coupling part 11 preferably will be glass sealed in both ends to 9 and 15 and part 21 respectively will be sealed to 15 and 19. Thus the material in 11 has to match the thermal expansion of both 9 and 15 and respectively the material in 21 has to match the thermal expansion of 15 and 19. One option is to extrude these connec-

tion parts 11 and 21 with a gradual change in composition of material such that the material in the end of 11 connected to 9 matches its thermal expansion, respectively the other end of 11 matches the thermal expansion of 14. In the same way 21 also could be made in such a way that thermal expansion is matching material in both 15 and 19 to prevent cracks. Also the inlet plenum room for air, unit 7 could be glass sealed to the low temperature heat exchanger 9 to ensure minimum leakage. Thus also the material in 7 has to match the thermal expansion of 9. In the same way the outlet plenum 23 for oxygen depleted air might be glass sealed to 18 and 19 and thus 23 has to be made of a material that matches 18 and 19 in thermal expansion. Part 7 is in the inlet end (incoming air) made of a round shape (pipe) to make it easier to fit into a flexible sealing 5. Respectively this is also done for the outlet plenum 23 (of the oxygen depleted high temperature air). Also here, in same way as inlet, a ring sealing, 24 is shown. For a vertical orientation as shown in Figure 7 a lower flexible sealing may not be necessary. This end could be fixed and thermal expansion allowed to take place in the upper end through the flexibility of seal 5. Thus, in at least one end, a sealing that allows expansion in the longitudinal direction has to be included. In the present invention this is solved by designing the inlet and/or outlet connectors 4 and 25 in a round shape (pipe end). Thus this makes it easier to have a flexible sealing. Flexible sealing rings 5 and 24 have to be made of a temperature resistant material (ceramic or metal). Also other flexible "pipe" sealing systems is possible.

The inlet and outlet pipes 4 and 25 may have the same shape to simplify the fabrication. Inlet pipe 4 leads the air stream to the inlet plenum made up by 7 and made in such a way that flexible sealings 5 can be mounted. The inlet pipe 4 is most preferably made of a material that also acts as a thermal barrier or lining between the hot inlet air and the outer metal pipe connected to the pressure vessel shell. This is especially important for the outlet pipe 25 in the high temperature end. Also shown are parts 6 and 22 that act as a thermal barrier or lining between exhaust/sweep gas and the flanged inlet/outlet metal pipe of the pressure vessel.

Also shown is the thermal barrier and insulation 3 between the high temperature inner parts and the outer metal wall or shell of the pressure vessel. Keeping a low temperature ($<500^{\circ}\text{C}$) in the outer pressure shell will reduce heat loss and allow the pressure shell to be made of a common engineering material (i.e. carbon steel). By lowering the temperature, the thickness of the wall and thus also the total weight of the device is reduced. This is important for an offshore installation.

Parts 3 are also made in a shape and of such a material that it can act as support for the inner parts. 2 is a layer of a flexible material between the inner wall (pressure shell) and 3 allowing for some movement caused by thermal expansion.

Figure 8.1 shows one embodiment of the device according to the present invention where the device is integrated with gas turbines.

Figure 8.2 shows another embodiment of integrating the reactor with gas turbines where more than one reactor have a common combustion chamber.

According to the present invention one or more reactor units can be coupled together and share a common combustion chamber as shown in Figure 8.1. This will allow multiple production of standard sized reactors and a cost efficient production by increasing total power output (upscaling) by integrating or coupling standard sized reactors together as shown in Figure 8.2. If for example the single device in the plant as shown in Figure 8.1 is producing 10 MW of power, the plant shown in Figure 8.2 having 6 reactors of the same size as a standard single reactor the plant will produce about 60 MW.

Shown in Figure 8.1 are two different alternatives for discharging the bleed stream. One alternative (Alt. 1) is to discharge a bleed stream from the cold part of the sweep gas loop. The bleed stream will have a temperature that allows it to be

sent directly to a steam turbine. The bleed stream taken out as shown in alternative one contains oxygen and this process stream can thus be used for further heat generation in a nitrogen free atmosphere and further as a heat source in an endothermic process. In alternative two (Alt. 2) a bleed stream is discharged after the combustion and thus it is almost oxygen free and at a high temperature level. If a steam turbine is to be used to enhance power generation from this stream, the temperature must be lowered, i.e. by injecting water. The bleed stream can be discharged anywhere in the sweep gas stream loop. Also shown in Figure 8.1 is that the inlet air pipe (from compressor to reactor) is longer than outlet lean air pipe (from reactor to turbine). This is found advantageous due to the higher temperature of the outlet oxygen lean air stream compared to the inlet air stream.

Figure 9.1 shows the device according to the present invention with the flow direction of the different gas streams. The figure shows that an oxygen containing gas stream (AN-030), preferably a compressed air stream, is fed to the heat exchange module (H-01) where the gas stream is heated before entering the mixed conducting membrane module (X-01). Oxygen is transported through the membrane wall to be picked up by the sweep gas stream (EG-030). An oxygen enriched sweep gas stream leaves the module (X-01) now named (EGO-010).

A part of the total fuel, (NG-030), is mixed with stream (EGO-010) in an additional combustion chamber (F-02) situated between (X-01) and (H-01) where the heat generated from this combustion will be supplied to heat exchanger (H-01) for heating incoming air. It has to be emphasized that the present invention will work without this combustion chamber (F-02) as explained in Figure 6. For this embodiment the sweep gas stream (EGO-020) entering the heat exchanger (H-01) will have somewhat higher temperature than the stream (EGO-010) and somewhat lower content of oxygen. The sweep gas stream (EGO-020) is then fed to the heat exchanger (H-01) for heating incoming air to the MCM-module (X-01). The

sweep gas stream (EGO-030) leaving (H-01) has now its lowest temperature and is supplied to the main combustion chamber (F-01) outside the reactor where most of the fuel (NG-020) is burned. A pressure booster (I-01) is installed close to the inlet of the main combustion chamber (F-01). The pressure increase from (EGO-030) to (EGO-040) enhanced by the pressure booster (I-01) is to ensure circulation in the sweep/exhaust gas loop.

A part of the hot exhaust gas (EG-040) is discharged as a bleed stream to prevent accumulation of mass in the exhaust/sweep gas loop. In principle the bleed gas stream (EG-040) can be discharged anywhere in the sweep gas circulation loop. For example it can be discharged in the cold end, from (EGO-030), and sent directly to a steam turbine. The exhaust gas (EG-020) is fed via the high temperature heat exchanger (H-02) to the membrane module (X-01). Acting as sweep gas, (EG-030) is receiving oxygen transported through the membrane from the air side and further transports the oxygen to the combustion chamber. Thus a closed loop with a continuous combustion of a carbon rich fuel with O_2 in a CO_2 and H_2O rich atmosphere is obtained.

Figure 9.2 shows how the plenum inlet and outlet 7 and 23 and heat exchangers (H-01) and (H-02) and the MCM-module (X-01) can be built into one sealed unit. This is to illustrate one important feature of the present invention which is the flow direction or flow paths of the two main streams air and sweep gas that contributes to minimize the leakage between air and sweep gas stream. The air stream has a straight flow and flows directly through the inner closed rooms between the heat exchangers (H-01) and (H-02) and the MCM-module (X-01), while the sweep gas stream flows in and out of the open side slots of (H-01), (X-01) and (H-02). To ensure a pressure build up inside the reactor the sweep gas should be allowed to fill the open space of the reactor. This will ensure that only outer reactor shells have to be designed for withstanding total pressure of the process.

Table 1 below gives example of data for the process flows with numbers according to Figure 9.1. Inlet conditions for the air stream; 20 bar, 450°C and 79 kg/s. Oxygen transport through membrane is 6.12 kg/s (membrane area is installed according to this). Fuel is added to match the stoichiometry of the combustion reaction.

A further advantage will be to have a low pressure difference (<5 bar) between the air side and the sweep gas side, preferably with somewhat higher pressure on the sweep gas side. This will ensure, in case of leakage between the air stream and the sweep gas stream, that the direction of leakage will be from the sweep gas side (CO_2 and H_2O) into the air side. This will be less harmful than if air leaks into the combustion loop (sweep gas), especially from an environmental point of view because in case of nitrogen (air) leakage into combustion (sweep gas loop) the NO_x gas could be produced.

Further, a low pressure difference between air and sweep gas side will allow designing with thinner walls in monoliths and thus better heat and oxygen (only X-O_1) transfer. This will also result in lower weight.

Table 1 below gives example of data for the process flows with numbers according to Figure 9.1. Inlet conditions for the air stream; 20 bar, 450°C and 79 kg/s. Oxygen transport through membrane is 6.12 kg/s (membrane area is installed according to this). Fuel is added to match the stoichiometry of the combustion reaction.

Table 1

Stream tag no.:	AL-010	AL-020	AN-030	AN-050	EG-010	EG-020	EG-030	EG-040
Components:								
Mole Flow kmol/sec								
CH ₄	0	0	0	0	0.005724	0.004866	0.004866	0.000859
C ₂ +	0	0	0	0	0	0	0	0
CO ₂	0.00090	0.00090	0.00090	0.00090	0.68614	0.68322	0.68322	0.10292
N ₂	2.123768	2.123768	2.123768	2.123768	0.006194	0.006265	0.006265	0.000929
O ₂	0.3784649	0.3784649	0.5697220	0.5697220	0	0	0	0
Ar	0.0254891	0.0254891	0.0254891	0.0254891	0	0	0	0
H ₂ O	0.0120762	0.0120762	0.0120762	0.0120762	1.212909	1.030973	1.030973	0.1819364
Total Flow kmol/sec	2.640698	2.640698	2.731956	2.731956	1.91097	1.624324	1.624324	0.2866454
Total Flow kg/sec	72.88	72.88	79.00	79.00	62.31	44.47	44.47	7.85
Total Flow cum/sec	13.99	16.33	8.31	14.67	12.16	10.33	8.96	1.82
Temperature C	1019	1221	463	1000	1266	1266	1050	1256
Pressure bar	19.60	19.40	20.00	19.80	20.06	20.06	20.00	20.06
Enthalpy kJ/kmol	80140.18	36894.61	11691.54	29700.68	-240270	-240270	-250840	-240270
Enthalpy kJ/kg	1060.729	1286.197	404.3137	1027.1	-8776.913	-8776.913	-9162.846	-8776.913
Enthalpy kW	76577.1	93738.07	31940.78	81140.93	-459160	-390280	-407440	-68872.29
Entropy J/kmol-K	24739.17	29681.75	6514.543	25024.88	22507.69	22507.69	16111.08	22507.69
Entropy J/kg-K	862.4418	1034.747	225.2841	865.4033	822.1919	822.1919	651.9985	822.1919
Density kmol/cum	0.1815737	0.1555783	0.3286462	0.186165	0.1672019	0.1672019	0.1812482	0.1672019
Density kg/cum	5.208446	4.462768	9.503466	5.383335	4.303437	4.303437	4.96171	4.303437
Average MW	28.68503	28.68503	28.91701	28.91701	27.37522	27.37522	27.37522	27.37522

Stream tag no.:	EGO-010	EGO-020	EGO-030	EGO-040	NG-020	NG-030	OX-010 (*)
Components:							
Mole Flow kmol/sec							
CH ₄	0.004866	0	0	0	0.069675	0.001946	0
C ₂ +	0	0	0	0	0.0009874728	0.00029685977	0
CO ₂	0.58322	0.59091	0.59091	0.59091	0.00254	0.00007	0
N ₂	0.006265	0.005290	0.005290	0.005290	0.000904	0.000025	0
O ₂	0.1912572	0.1762761	0.1762761	0.1762761	0	0	0.1912572
Ar	0	0	0	0	0	0	0
H ₂ O	1.030973	1.045701	1.045701	1.045701	5.02105E-005	1.40470E-006	0
Total Flow kmol/sec	1.815581	1.818177	1.818177	1.818177	0.0836758	2.34093E-003	0.1912572
Total Flow kg/sec	50.59	50.63	50.63	50.63	1.68	0.05	6.12
Total Flow cum/sec	9.85	10.47	5.93	5.83	0.05	0.0015	0.97
Temperature C	1028	1093	505	511	34	34	1000
Pressure bar	19.80	19.80	19.75	20.25	36.00	36.00	21.00
Enthalpy kJ/kmol	-221900	-221700	-248760	-248530	-87413.69	-87413.69	32362.44
Enthalpy kJ/kg	-7964.114	-7960.869	-8932.566	-8924.502	-4353.816	-4353.816	1011.364
Enthalpy kW	-402870	-403080	-452280	-451880	-7314.411	-204.6293	6189.548
Entropy J/kmol-K	17971.26	20163.23	-6530.105	-5449.694	-122240	-122240	21762.67
Entropy J/kg-K	645.0031	724.0367	-198.5793	-195.6882	-6088.488	-6088.488	680.109
Density kmol/cum	0.1843344	0.1737103	0.3064727	0.3120345	1.533792	1.533792	0.1975274
Density kg/cum	5.135978	4.837547	8.53476	8.689646	30.7947	30.7947	6.32064
Average MW	27.86228	27.84835	27.84835	27.84835	20.07749	20.07749	31.9988

(*)

The oxygen flow (OX-010) is not a physical gas flow as shown in the table. Oxygen is transported through the membrane as oxygen ions and thus (OX-010) in Table 1 is for the purpose of calculation.

Claims

1. A device for combustion of a carbon containing fuel in a nitrogen free atmosphere,
said device comprising:
a hollow shell defining an enclosure having an inlet for said fuel, an inlet for a compressed oxygen containing gas stream, an outlet for discharging an oxygen depleted gas stream and an outlet for discharging a bleed stream;
one or more heat exchange modules arranged to heat the incoming compressed oxygen containing gas stream;
one or more mixed conducting membrane modules arranged to separate oxygen from said oxygen containing gas stream resulting in an oxygen rich gas stream and said oxygen depleted gas stream;
a first and possibly a second combustion chamber for combustion of said fuel having an inlet pipe connected to said inlet for fuel to convey fuel to said chamber, an inlet pipe connected to said heat exchange module(s) to convey hot oxygen rich gas to said chamber and an outlet pipe connected to said membrane module(s) to convey exhaust gas from the combustion chamber to the membrane module;
a pressure booster installed prior to the first combustion chamber;
means (11,21) for connecting said heat exchanger module(s) and membrane module(s);
means (7,23) for connecting said heat exchanger module(s) and said membrane module(s) to the inlet for the compressed oxygen containing gas stream and the outlet for the oxygen depleted gas stream and
a pipe to convey a part of said exhaust gas stream directly to said heat exchange module(s) and back to said outlet pipe from the combustion chamber.

2. A device according to claim 1,
said hollow shell further includes one or more reactor(s) which includes said heat exchanger module(s), said membrane module(s), said means (7,11,21,23), an outlet pipe for said hot oxygen rich gas stream, said outlet for discharged oxygen depleted gas stream, an inlet pipe for said exhaust gas and said inlet for compressed oxygen containing gas stream.
3. A device according to claim 1,
said hollow shell further includes one or more reactor(s) which includes said heat exchanger module(s), said membrane module(s), said second combustion chamber, said means (7,11,21,23), an outlet pipe for said hot oxygen rich gas stream, said outlet for discharged oxygen depleted gas stream, an inlet pipe for said exhaust gas and said inlet for compressed oxygen containing gas stream.
4. A device according to claim 1,
wherein said modules and said second combustion chamber are vertically interconnected one above the other.
5. A device according to claim 1,
wherein said modules are vertically interconnected one above the other.
6. A device according to claim 1,
wherein the membrane module is installed between two heat exchange modules.
7. A device according to claim 1,
wherein the second combustion chamber is installed between one of the heat exchange module and a membrane module.

8. A device according to claims 2 and 3,
wherein said outlet pipe for said hot oxygen rich gas stream is connected to the inlet pipe to the first combustion chamber and said inlet pipe for said exhaust gas is connected to the outlet pipe from the first combustion chamber.
9. A device according to claim 1,
said pressure booster is a fan or a compressor.
10. A device according to claim 1,
said heat exchange module(s) and said membrane module(s) comprises a multichannel monolithic structure.
11. A method for operating a device according to claims 1 to 10,
said method comprises the following steps:
a compressed oxygen containing gas stream is fed to a first heat exchange module where it is heated by means of heat generated by combustion of a fuel in a combustion chamber;
said heated gas stream is fed to a mixed conducting membrane module(s) where most of the oxygen is separated from said gas stream and an oxygen depleted gas stream is obtained;
a sweep gas is fed to said membrane module to pick up oxygen and the oxygen enriched sweep gas is further fed to a pressure booster;
the pressurized sweep gas stream enters the combustion chamber where it is mixed with a fuel for combustion;
and said oxygen depleted gas stream is fed to another heat exchange module for further heating before leaving said device.
12. A method for operating a device according to claim 11,
where the combustion product; the exhaust gas, is applied as sweep gas.

13. A method for operating a device according to claim 11 ,
where a part of the exhaust gas is taken out as a bleed stream to
prevent accumulation of mass in the device.
14. A plant for generation of power that implies reduced emission of
carbon dioxide and NOx to the atmosphere,
characterised in that
the device according to claims 1-10 is integrated with one or more gas
turbine(s).
15. A plant for performing an endothermic chemical reaction,
characterised in that
the device according to claims 1-10 is integrated with a plant performing
an endothermic reaction.
16. A process for generation of power that implies reduced emission of
carbon dioxide and NOx to the atmosphere,
characterised in that
the hot oxygen depleted air stream and/or the bleed gas stream leaving
the device according to claims 1-10 is fed to one or more gas turbines.
17. A process for supplying heat to an endothermic reaction,
characterised in that
the hot oxygen depleted air stream and/or the bleed gas stream leaving
the device according to claims 1-10 is fed to the plant performing the
endothermic reaction.

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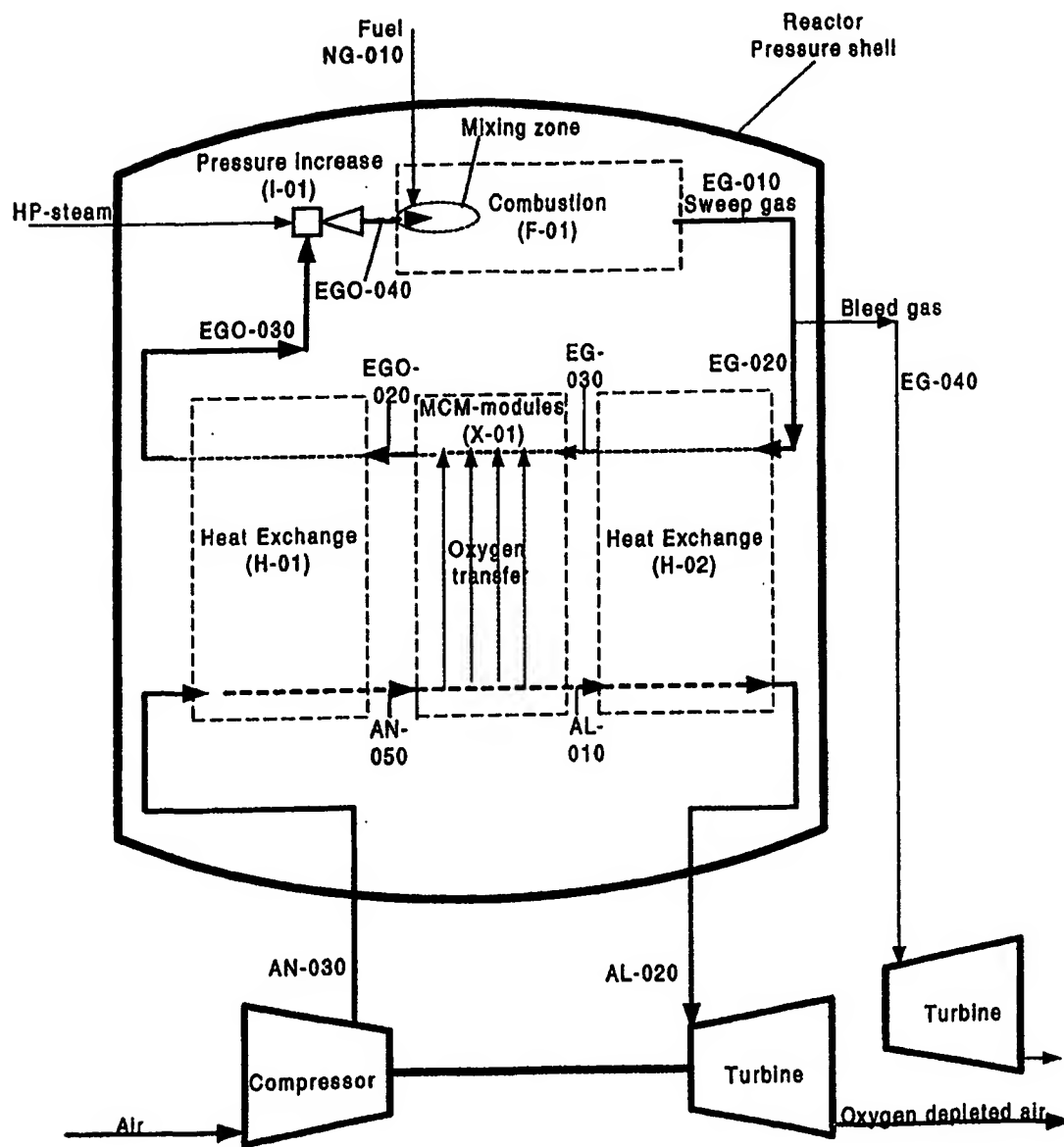


Fig. 1

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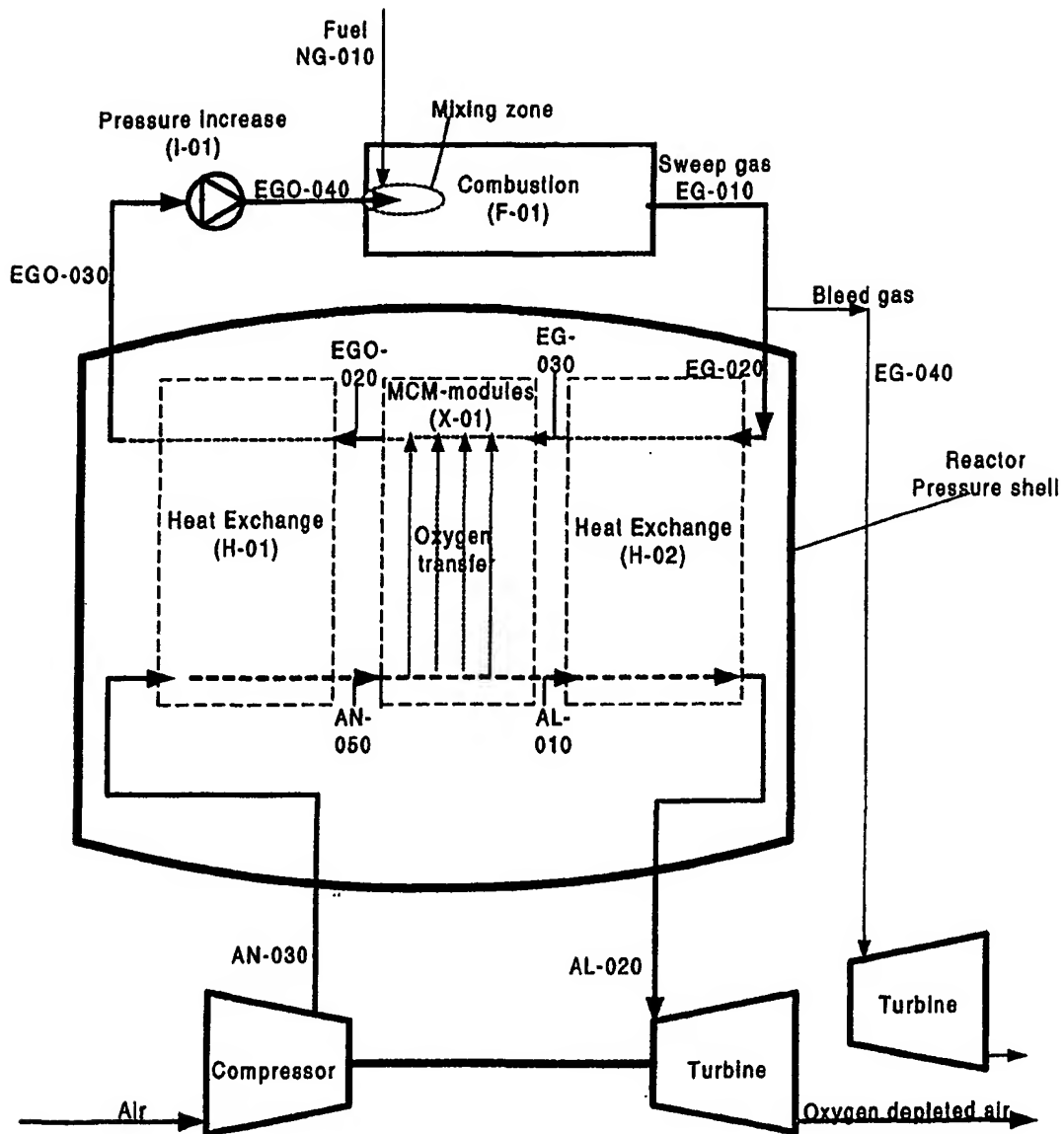


Fig. 2

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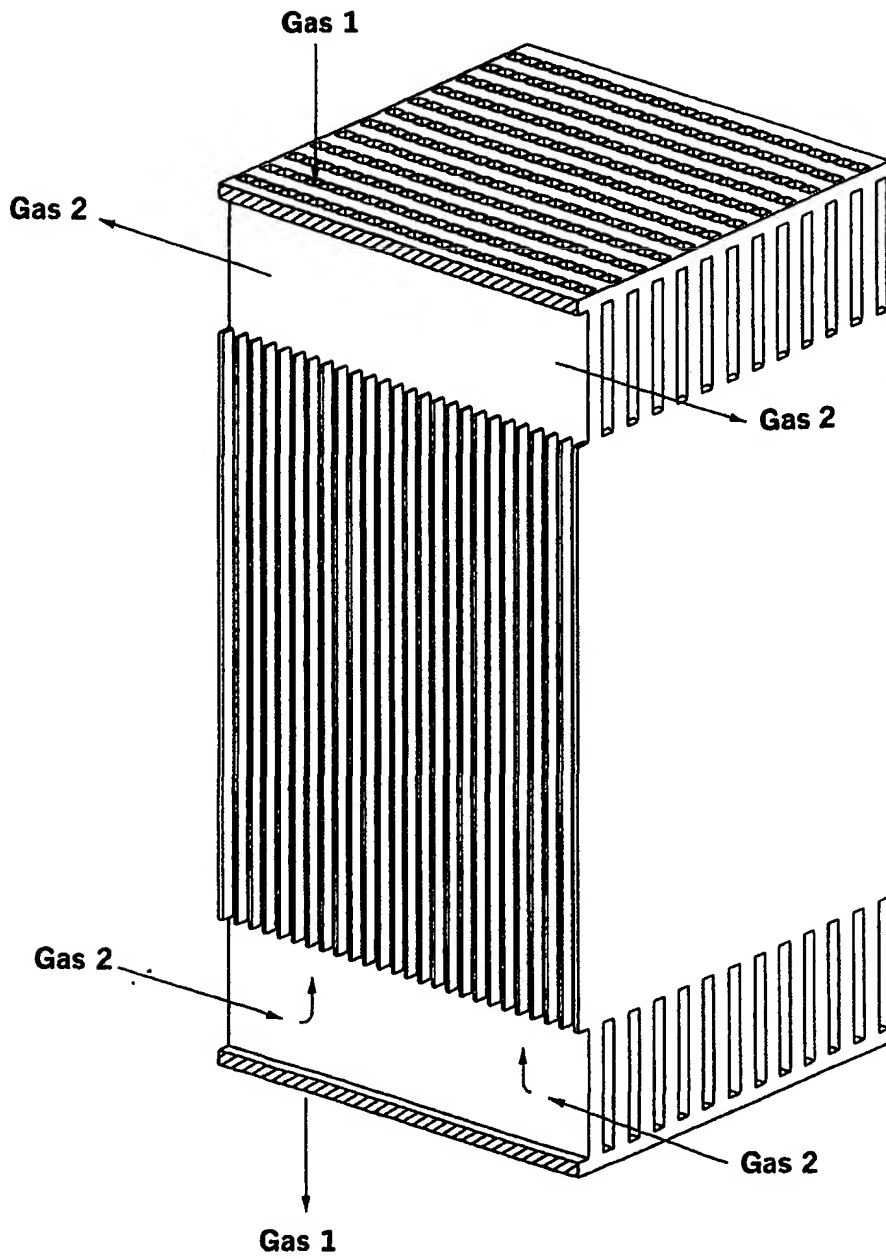


Fig. 3

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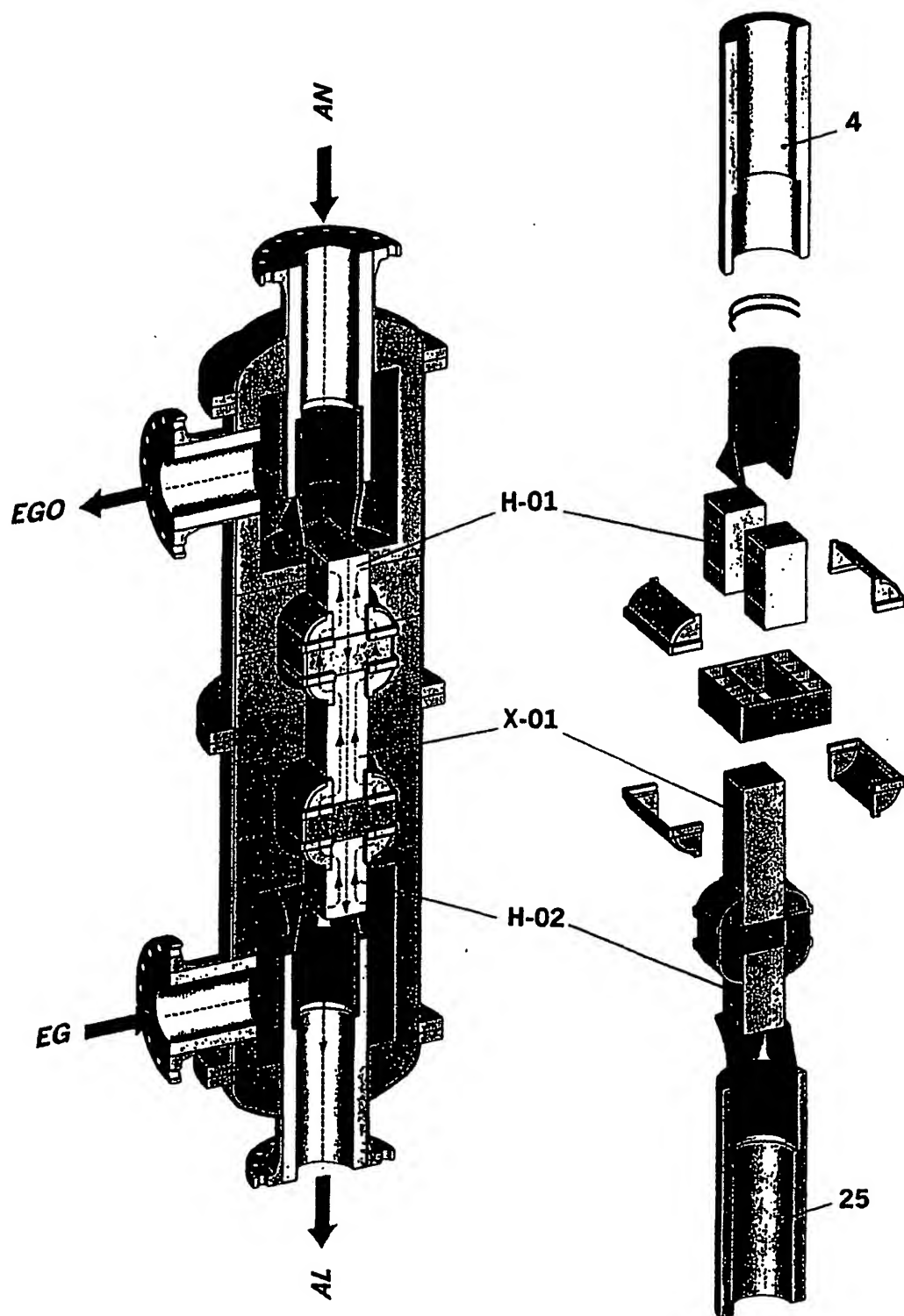


Fig. 4

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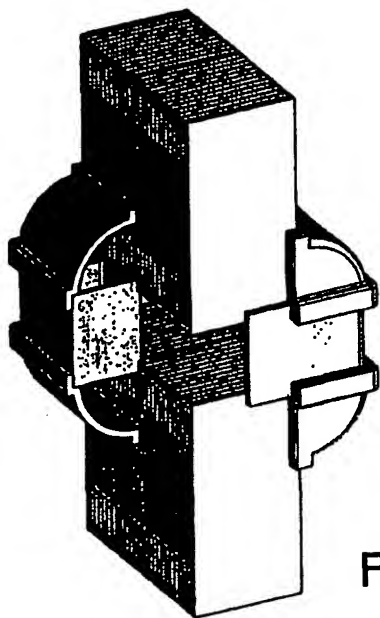


Fig. 5.1

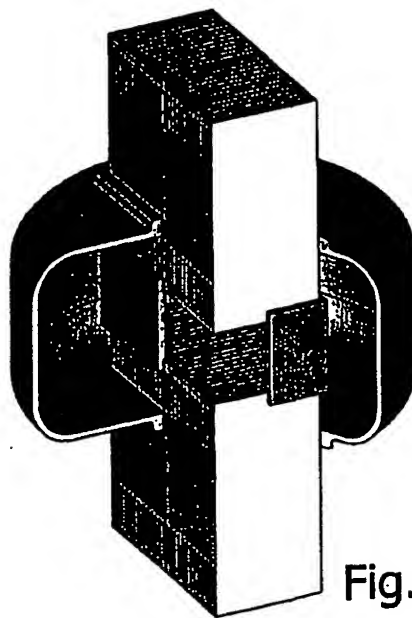


Fig. 5.2

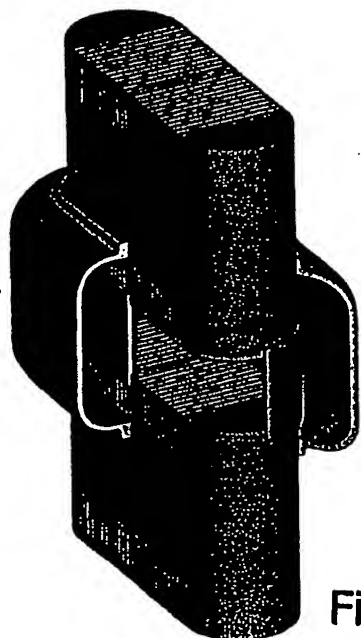


Fig. 5.3

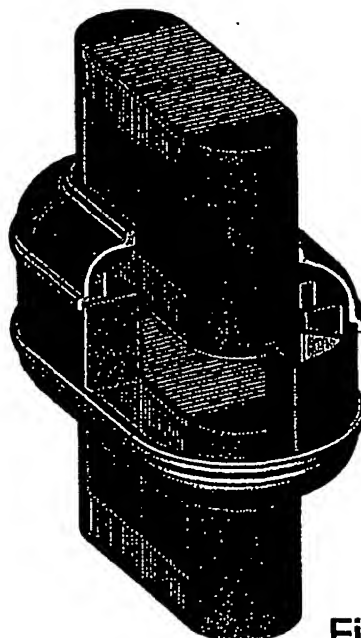


Fig. 5.4

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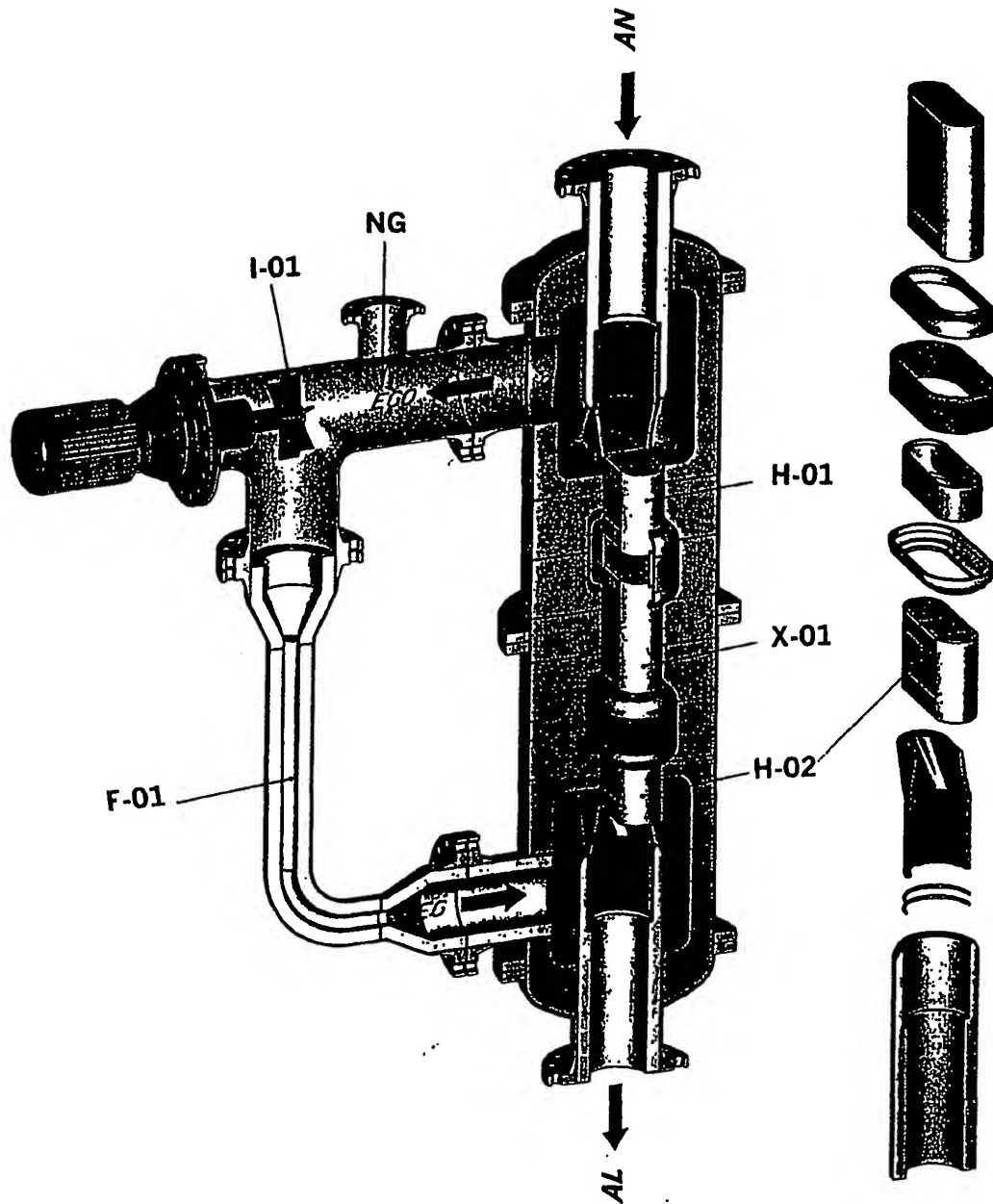


Fig. 6

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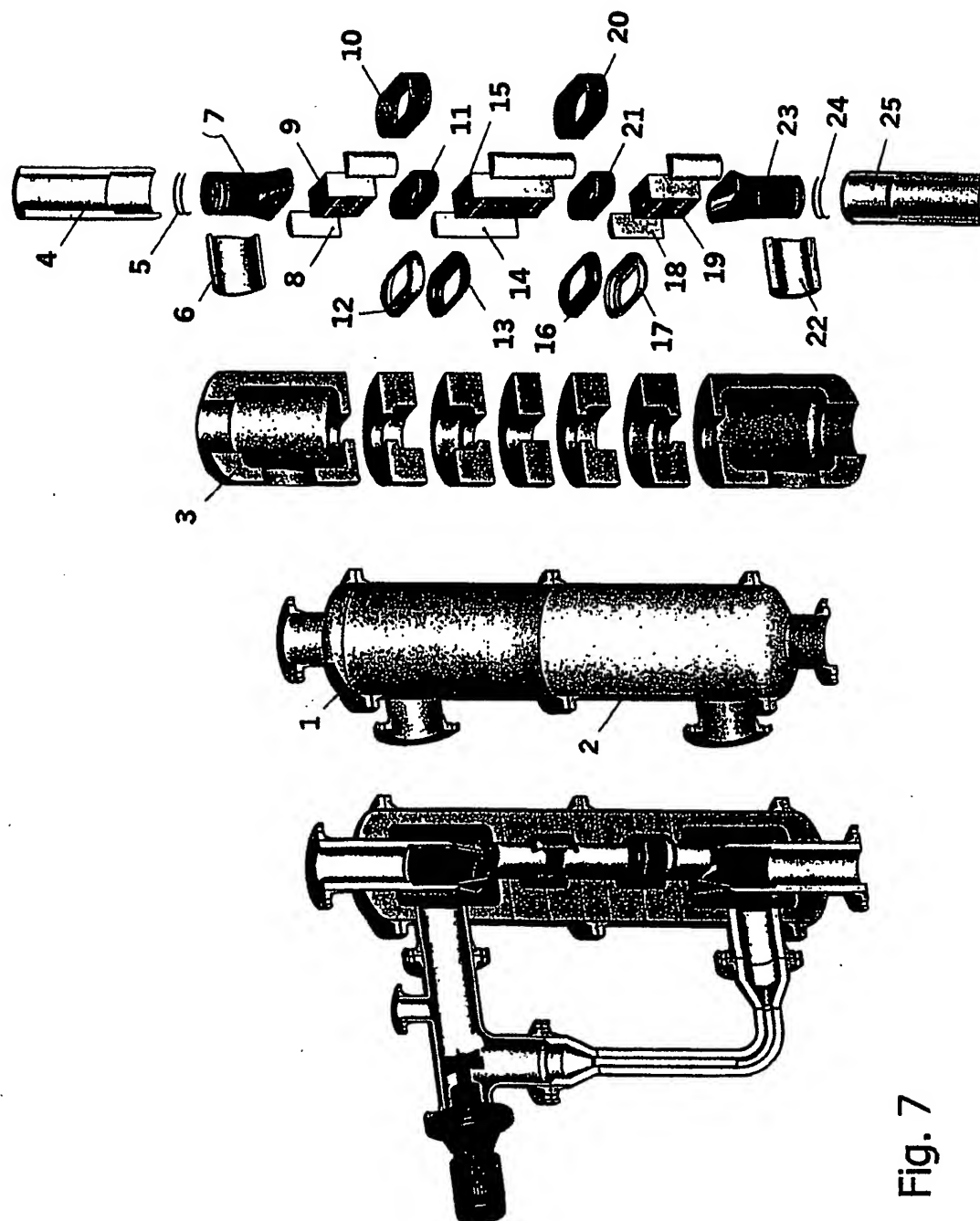


Fig. 7

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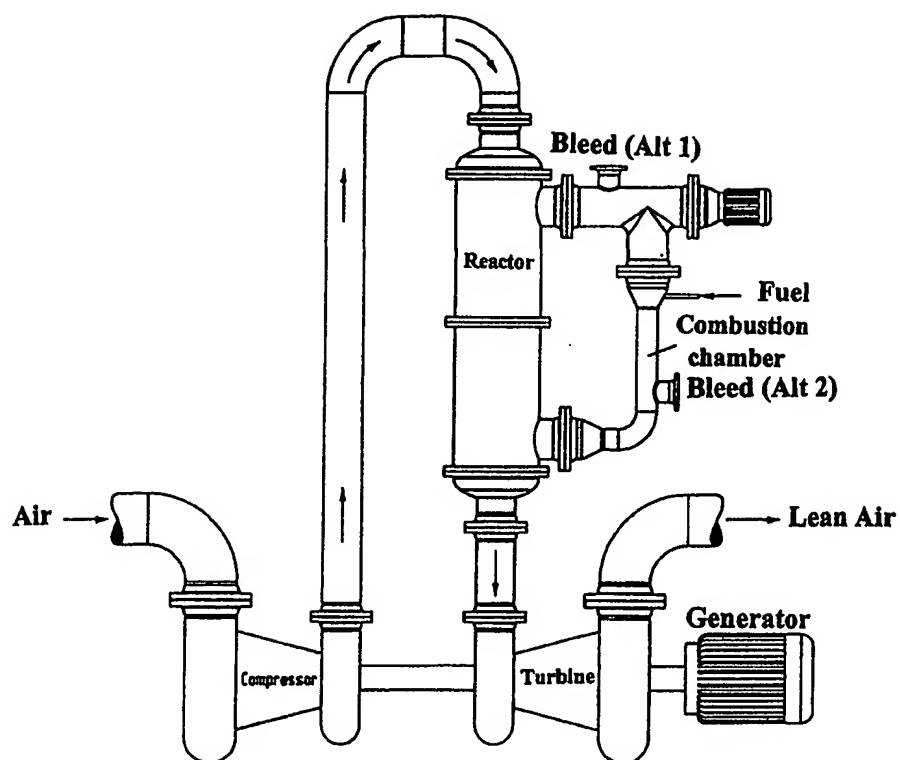


Fig. 8.1

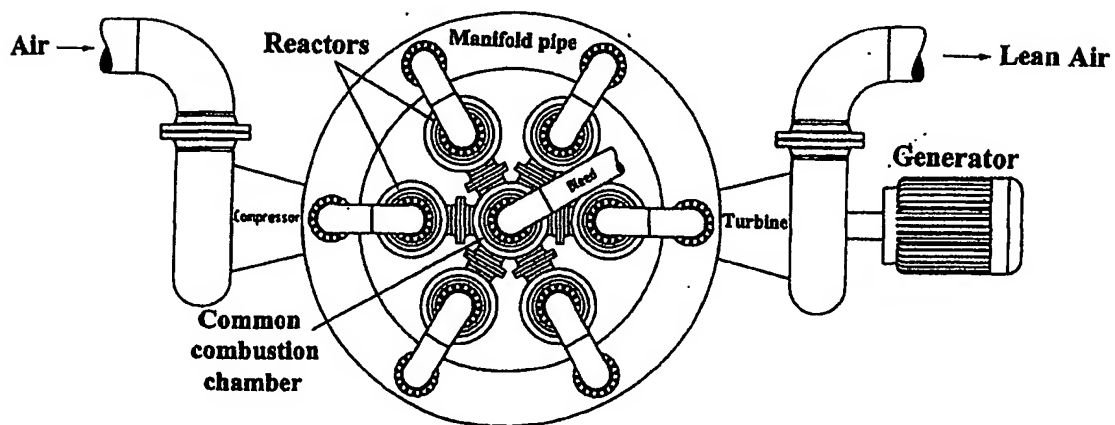


Fig. 8.2

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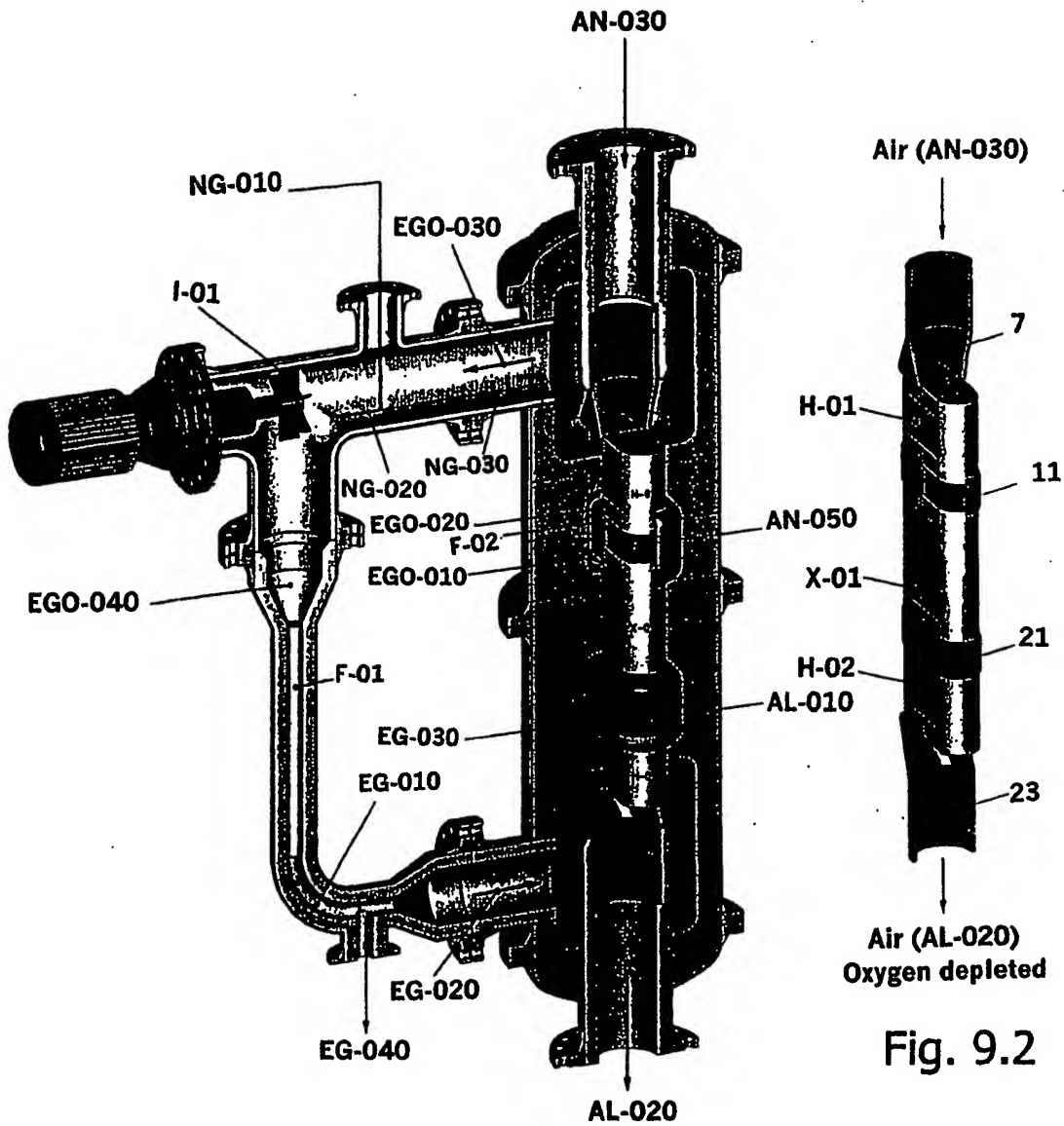


Fig. 9.1

Fig. 9.2

1
INTERNATIONAL SEARCH REPORT

International application No.

PCT/NO 01/00499

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: F23C 9/00, F23L 7/00, B01D 53/22, F02C 3/34

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: F23C, F23L, F02C, B01D, F23G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1040861 A1 (PRAXAIR TECHNOLOGY, INC.), 4 October 2000 (04.10.00), page 7, line 34 - line 51, figure 1 --	1-17
X	WO 0033942 A1 (NORSK HYDRO ASA), 15 June 2000 (15.06.00), page 10, line 1 - line 5, figures 1,2, claims 1-3 --	1-17
X	WO 9855208 A1 (NORSK HYDRO ASA), 10 December 1998 (10.12.98), figures 1-4, abstract --	1-17
X	EP 0882486 A1 (PRAXAIR TECHNOLOGY, INC.), 9 December 1998 (09.12.98), figure 1, claims --	1-17

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Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

Information on patent family members

28/01/02

International application No.

PCT/NO 01/00499

Patent document cited in search report			Publication date	Patent family member(s)		Publication date
EP	1040861	A1	04/10/00	AU	2259200 A	05/10/00
				BR	0001491 A	23/01/01
				CA	2302143 A	29/09/00
				CN	1269488 A	11/10/00
				JP	2000304206 A	02/11/00
				US	6149714 A	21/11/00
				ZA	200001543 A	16/10/00
WO	0033942	A1	15/06/00	AU	3540699 A	26/06/00
				EP	1146951 A	24/10/01
				NO	308401 B	11/09/00
				NO	985706 A	05/06/00
WO	9855208	A1	10/12/98	AU	4139097 A	21/12/98
				EP	0993332 A	19/04/00
				JP	2001509878 T	24/07/01
				NO	308400 B	11/09/00
				NO	972632 A	07/12/98
				US	6298664 B	09/10/01
EP	0882486	A1	09/12/98	AU	738862 B	27/09/01
				AU	6992098 A	10/12/98
				BR	9801784 A	03/08/99
				CA	2239677 A	05/12/98
				CN	1220181 A	23/06/99
				JP	10339405 A	22/12/98
				US	5888272 A	30/03/99
				US	6149714 A	21/11/00
				ZA	9804852 A	04/01/99

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